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"Kinetic Study of Ion-sensitized Terminations of
Radical Polymerisation"

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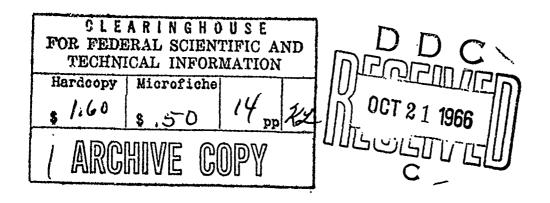
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Abstract

A kinetic study of the polymerisation of acrylamide
initiated by the thermal catalyst 4-4'-azo-bis-4-cyanopenta-
noic acid has shown that up to 10% conversions the rate of
polymerisation is directly proportional to the concentration
of monomer and to the square root of the concentration of
catalyst.   In the presence of ferric perchlorate and deci-
molar perchloric acid, however, the overall rate of poly-
merisation is reduced and the rate now becomes directly pro-
portional to the first power of the catalyst concentration
and inversely proportional to the concentration of ferric ions
present.

Acrylamide is readily polymerised by a variety of agents capable of producing radicals at the rate of about 10^{-10} mole per litre per sec., although relatively few kinetic studies of this polymerisation have in fact been made. In those which have been undertaken, polymerisation has been initiated by the action of ionising radiation (1), the action of ultrasonic waves (2), by the use of oxidation- reduction systems (3) and by photochemical methods (4). None of these methods are ideally suited to the investigation reported here, which employs the thermal catalyst, 4-4'-azo-bis-4-cyanopentanoic acid, 10^{-4} M solutions of which are capable of initiating the polymerisation of acrylamide at room temperature.

Preparation and purification of materials

The catalyst, 4-4'-azo-bis-4-cyanopentanoic acid, was prepared from levulic acid by a modified Strecker-type reaction using hydrazine hydrate and sodium cyanide followed by oxidation with bromine. It seems to be important to carry out this oxidation very slowly and to keep the temperature near to 0° C. The product was purified by suspending it in water at 60° and then adding sodium carbonate until all the solid just dissolved. This solution was then cooled and acidified with hydrochloric acid, the precipitated 4-4'-azo-bis-4-cyanopentanoic acid being filtered off and dried in vacuo over anhydrous calcium chloride. Equivalent weight of the product as determined by titration with standard alkali was 141.2 ± 0.2 (theory = 140.1). We found it necessary to re-purify the catalyst at frequent intervals if satisfactory kinetic results were to be obtained.

Acrylamide was crystallised twice from chloroform and then washed with benzene. Finally it was placed in a vacuum desiccator, which was pumped out through a cold trap until all traces

of solvent had been removed: m.p. (uncorr.) $84.0 \pm 0.5^{\circ}$ (Lit. 84.5 ± 0.3).

Water used as solvent in kinetic experiments was purified by distillation followed by percolation through Amberlite monobed resin MB-1 (5) and had a specific conductance of less than 10^{-6} mhos at room temperature.

Solutions of ferric salts used were obtained by dissolving ferric hydroxide in excess of the appropriate pure acid. Ferric hydroxide itself was purified by two successive precipitations with ammonia (analytical reagent grade) and by washing with purified water.   Constant boiling perchloric acid (analytical reagent grade) was distilled in vacuo before use.   The final iron content of solutions obtained was determined both gravimetrically and by titration.   Concentrations of hydrogen ions were obtained by titration with standard alkali using phenolphthalein as indicator and by making the necessary correction for the presence of the iron salt.

Kinetic measurements

Rates of polymerisation have been measured either by precipitating and weighing the polymer produced (gravimetric method) or by measuring in a suitable dilatometer the contraction in volume during polymerisation.   The deaeration procedure employed was the same for both methods.

Known volumes of monomer and catalyst solutions of known concentration were placed in separate vessels connected by an inverted U-shaped tube, which in turn was fused to one arm of a T-piece.   Of the remaining limbs of the T-piece, one was attached to a vacuum line and the other either connected to a dilatometer or sealed off as required.   The dilatometer

consisted of a spherical bulb of about 15 ml. capacity sealed
to a length of precision 1 mm. bore capillary tubing.

Solutions were deaerated two or three times at pressures
of $10^{-4} - 10^{-5}$ mm. Hg, after which the connexion to the vacuum
line was sealed off and the whole deaeration unit transferred
to a thermostat operating at $25.00 \pm 0.02^{\circ}$ C.   When reactants
had attained thermostat temperature, they were thoroughly mixed
and either transferred to the dilatometer, which was then
removed from the deaeration unit, or returned to the thermostat
for a suitable period of time.   In the gravimetric method,
polyacrylamide was precipitated from solution by the gradual
addition of either ethanol or dioxan (6) and was dried to con-
stant weight in vacuo over anhydrous calcium chloride at room
temperature.   In both methods no observations were made for
conversions greater than 10%.

TABLE   1

Effect of variation in monomer concentration
on rate of polymerisation.

Monomer concn. $[m_1]$	$10^4.Rp$ (mole litre^{-1} min.$^{-1}$)		$10^4.Rp/[m_1]$	
	Gravimetric method	Dilatometry	Gravimetric method	Dilatometry
0.640 M	6.90	7.90	10.8	12.3
0.528	6.42	6.30	12.2	11.9
0.419	4.52	–	10.8	–
0.407	–	4.16	–	10.2
0.313	–	3.78	–	12.1

Catalyst concentration $= 1.64 \times 10^{-4}$ M.

A comparison of the rates of polymerisation obtained with similar concentrations of monomer and catalyst by the two methods employed is given in Table 1. Rates quoted for the dilatometric method have been evaluated using a shrinkage factor of 0.050 millimoles of acrylamide polymerised for each 1 mm. contraction in a 1 mm. diameter capillary (7). Analysis of the kinetic data given in Table 1 by the method of least squares shows Rp to be proportional to $[m_1]^{1.04}$, which indicates that within the limits of experimental error, the rate of polymerisation is directly proportional to the first power of concentration of acrylamide. Average values of the ratio $10^4 Rp/[m_1]$ given in the final columns of Table 1 are 11.6 ± 0.7 and 11.3 ± 0.6 for the dilatometric and gravimetric methods respectively. This agreement provides satisfactory confirmation for the value of the shrinkage factor used in computing rates from dilatometric data.

The effect of variation in the catalyst concentration on the rate of polymerisation is shown by the kinetic results given in Table 2, analysis of which by the method of least squares shows Rp to be proportional to $[Cat]^{0.49}$. Thus, within the limits of experimental error, the rate of polymerisation of acrylamide has been shown to be proportional to the square root of the concentration of catalyst, the mean value of $Rp/[Cat]^{\frac{1}{2}}$ being 5.04 x 10^{-2} with a mean deviation of ± 0.29 x 10^{-2}; the value of $Rp/[m_1][Cat]^{\frac{1}{2}}$ obtained is 9.55 x 10^{-2}. This should be compared with a value of 8.94 x 10^{-2} calculated for this ratio from the kinetic data given in Table 1 for a <u>constant</u> concentration of catalyst.

TABLE 2

Effect of variation of catalyst concentration on rate of polymerisation

10^4 Catalyst concn. $[Cat]$	10^4 Rp (mole litre^{-1} min.$^{-1}$)	10^2 Rp/$[Cat]^{\frac{1}{2}}$
0.096	1.78	5.74
0.548	3.51	4.74
0.835	4.80	5.25
0.866	4.92	5.28
1.43	5.38	4.52
1.64	6.42	5.01
1.64	6.86	5.36
1.64	6.30	4.92
2.60	7.30	4.55
3.34	9.24	5.05

$$[m_1] = 0.528M$$

Measurements of molecular weight

Average molecular weights of the polymers produced under the conditions employed in our kinetic experiments have been calculated from measurements at 25.0° C. of the viscosity of aqueous solutions containing known concentrations of polymer. Unfortunately, once precipitated, polyacrylamide can only be re-dissolved in water with extreme difficulty. Polymer solutions, obtained by the same procedure as that adopted in the kinetic experiments (except that larger volumes of monomer and catalyst solutions of known concentration were employed), were used after suitable dilution in our measurements of viscosity.

The concentration of polymer present in these solutions was determined by precipitating it with dioxan, filtering off and weighing.

Viscosities were measured with a U-tube viscometer, which had been previously calibrated against water and nitrobenzene, the equation

$$10^5 \eta = 20.2 \, d.t - 3560 \, d/t$$

being used to compute viscosity (η) in poises from the time of flow (t) in seconds and the density (d) of the solution. A small correction for the presence of unchanged monomer was applied in the calculation of specific viscosities (η_{sp}). The data given in Table 4 show that η_{sp}/c, where c is the number of grams of polymer per 100 ml. of solution, is itself a linear function of polymer concentration, so that intrinsic viscosities $[\eta]$ may be readily obtained by graphical extrapolation to c = 0.

TABLE 3

Density of aqueous solutions of acrylamide at 25.0° C.

gm./100 ml. solution	2.7408	3.7500	6.9776	10.7896
density (gm./ml.)	0.9986	0.9999	1.0034	1.0062

Several relationships connecting intrinsic viscosity with average molecular weight have been suggested for polyacrylamide (3,9). Of these, the following equation

$$[\eta] = 6.8 \times 10^{-4} \, \bar{M}_N^{0.66}$$

obtained by Collinson, Dainton and McNaughton (8) has been used to compute the number-average molecular weights given in Table 5.

TABLE 4

Variation of specific viscosity with polymer concentration

(a) $Rp = 9.24 \times 10^{-4}$ mole litre^{-1} min.$^{-1}$ $[Cat] = 3.34 \times 10^{-4}$ M.

10^2 c	9.46	6.61	4.33	2.64	0
η_{sp}/c	25.4	23.6	21.5	20.0	17.6

(b) $Rp = 6.86 \times 10^{-4}$ mole litre^{-1} min.$^{-1}$ $[Cat] = 1.64 \times 10^{-4}$ M.

10^2 c	4.81	4.18	3.66	2.73	0
η_{sp}/c	21.5	21.3	19.6	19.3	16.2

(c) $Rp = 4.80 \times 10^{-4}$ mole litre^{-1} min.$^{-1}$ $[Cat] = 0.835 \times 10^{-4}$ M.

10^2 c	5.99	4.25	2.55	0
η_{sp}/c	21.0	19.2	17.2	14.4

TABLE 5

Average molecular weights of polyacrylamide

10^4 $[Cat]$	3.34	1.64	0.835
$[\eta]$	17.6	16.2	14.4
10^{-6} $\bar{M}_N$	4.85	4.29	3.57

Effect of ferric salts on kinetics of polymerisation

Aqueous solutions of ferric salts are subject to a series of complex hydrolytic equilibria. Such solutions must, therefore, be allowed to attain a state of equilibrium before use, a process which may require a substantial period of time for its completion (10). In the present experiments, a minimum period of ten days was required if consistent results were to be obtained. We now believe that certain values of Rp measured in the presence of $FeCl_3$ and quoted previously may be too low possibly because an insufficient period of time was allowed for the attainment of equilibrium. The procedure adopted in these experiments was to allow solutions containing the required amounts of ferric and hydrogen ions to equilibrate over a minimum period of ten to twelve days, and then to dissolve in them the requisite quantity of monomer just before use. This precaution is necessary if hydrolysis of acrylamide during the equilibration period is to be avoided. Solutions containing the catalyst were arranged to be identical in composition in respect of both iron and acid, so that no change in their concentrations occurs on mixing the reactants. The deaeration and kinetic procedures were the same as that already described.

Rates of polymerisation obtained in the presence of varying concentrations of ferric perchlorate are summarised in Table 6, and analysis of these data by the method of least squares shows Rp to be <u>inversely</u> proportional to $\left[Fe^{3+}\right]_0^{0.97}$ (the subscript zero indicates initial concentration). In a similar way the data given in Table 7, which refer to a constant concentration of ferric perchlorate, show that in the presence of this salt, Rp is now directly proportional to $\left[Cat\right]^{0.95}$, so that within the limits of experimental error we may take the rate of polymerisation to be proportional to the ratio $\left[Cat\right]/\left[Fe^{3+}\right]$, the

TABLE 6

Effect of ferric perchlorate on rate of polymerisation

10^5 Fe(ClO$_4$)$_3$ concn. $[Fe^{3+}]$	10^4 Rp (mole litre^{-1} min.$^{-1}$)	10^5 Rp$[Fe^{3+}]/[Cat]$
0	18.5	–
2.78	18.3	12.7
4.64	10.6	12.2
4.64	10.5	12.2
18.56	2.85	13.2

$[monomer]$ = 1.00M. $[Cat]$ = 4.01 x 10^{-4}M. $[H_3O^+]$ = 0.11M.

TABLE 7

Effect of variation of catalyst concentration on rate of polymerisation in presence of ferric perchlorate.

10^4 Catalyst concn. $[Cat]$	10^4 Rp (mole litre^{-1} min.$^{-1}$)	10^5 Rp$[Fe^{3+}]/[Cat]$
1.50	1.92	11.9
2.00	2.62	11.7
2.60	2.96	10.6
2.60	2.98	10.6
3.51	4.53	12.0
4.51	5.06	10.4
5.51	6.81	11.5

$[monomer]$ = 1.00M. $[Fe^{3+}]_0$ = 9.28 x 10^{-5}M. $[H_3O^+]$ = 0.11M.

average values of $Rp[Fe^{3+}]/[Cat]$ being $12.6 \pm 0.4 \times 10^{-5}$ and $11.2 \pm 0.6 \times 10^{-5}$ for the data in Tables 6 and 7 respectively.

These results demonstrate that in the presence of ferric perchlorate, the normal quadratic termination step of the polymerisation process is effectively replaced by one which is first order with respect to ferric ion.   In this connexion we have shown that some reduction to the ferrous condition occurs during polymerisation.   From these observations it may be concluded that in the presence of a sufficient concentration of ferric salt, the growing polymer chains are exclusively terminated by electron transfer from a ferric ion to a polymeric radical.   The net result of this mode of termination is a significant reduction in the overall rate of polymerisation, as can be seen by comparing the first entry in Table 6 with those below it, and a change from one-half to one in the order of the reaction with respect to catalyst.

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